IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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In re Application of: :
Y. Taka et al. Art unit: 1774
Serial No. 10/699,343 :
Filed: 10/30/2003
For: INK-JET RECORDING SHEET :

_____x

DECLARATION

Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

Sir:

I, Tsutomu YOSHII hereby declare and say as follows:

I am familiar with both the English and Japanese languages and I have compared the annexed English translation with the Japanese text of Japanese Patent Application No. 324623/2002.

To the best of my knowledge and belief, the annexed English translation is an accurate translation of the above Japanese application.

The undersigned declares further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like

so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the U.S. Code and that such willful false statements may jeopardize the validity of the above-identified application or any patent issuing thereon.

Tsutomu YOSHII

Dated: This 23rd day of May, 2005.

Patent Application No. 324623/2002

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Title of Document:	Specification	1
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[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION]

INK-JET RECORDING SHEET

[CLAIMS]

[Claim 1] An ink-jet recording sheet comprising a support and an ink accepting layer provided on at least one side of the support wherein the ink accepting layer is a porous ink-accepting layer comprising a hydrophilic binder containing a polymer compound crosslinked by irradiation of ionizing radiation, micro particles, and at least one component selected from the group consisting of (A) a nitrogen-containing compound, (B) a sulfur-containing compound, (C) a polyvalent metal salt and (D) a phenol compound.

[Claim 2] The ink-jet recording sheet of Claim 1, wherein the micro particles have an average diameter of from 5 to 200 nm.

[Claim 3] The ink-jet recording sheet of Claim 1 or 2, wherein a ratio of the contained micro particles to the hydrophilic binder is from 2 to 50 by weight.

[Claim 4] The ink-jet recording sheet of Claim 3, wherein the ratio of the contained micro particles to the hydrophilic binder is from 5 to 15 by weight.

[Claim 5] The ink-jet recording sheet of any one of Claims 1 to 4, wherein the polymer compound crosslinked by irradiation by ionizing radiation is a polymer compound formed by crosslinking a hydrophilic resin having a dimer formable photosensitive group formed by irradiation via ionizing radiation.

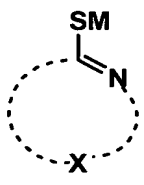
[Claim 6] The ink-jet recording sheet of anyone of Claims 1 to 5, wherein the nitrogen-containing compound is at least one selected from the group consisting of a hindered amine compound, a hydroxylamine compound and a water-soluble aliphatic tertiary amine compound.

[Claim 7] The ink-jet recording sheet of any one of Claims 1 to 5, wherein the sulfur compound is a compound represented by Formula 1 or Formula 2:

Formula 1 R-S-R'

wherein R and R' are each an alkyl group or an aryl group,

Formula 2



wherein M is a hydrogen atom, an ammonium ion or a metal atom; X is a group of non-metal atoms necessary to form a five- through seven-member ring.

[Claim 8] The ink-jet recording sheet of any one of Claims 1 to 5, wherein the polyvalent metal salt is a water-soluble salt of one selected from the group consisting of cesium, magnesium, aluminum and zirconium.

[Claim 9] The ink-jet recording sheet of any one of Claims 1 to 5, wherein the phenol compound is a hindered phenol compound or a hydroquinone diether compound.

[DETAIL DESCRIPTION OF THE INVENTION]

[0001]

[FIELD OF THE INVENTION]

The present invention relates to an ink-jet recording sheet, hereinafter also referred simply to as a recording sheet.

[0002]

[CONVENTIONAL ART]

The quality of printed images via ink-jet printing is being made equal to that of prints formed by silver halide photography, due to rapid progress of technology of ink-jet recording. The quality of images formed by ink-jet printing depends on the printer, ink and recording sheet. Regarding

image quality, the contribution of technological innovation of the former two is significant. Consequently, the importance of the quality of the recording sheet is made to be considerably higher.

[0003]

Hitherto, various improvements have been applied to recording sheets to obtain printed image quality approaching that of photographic prints. Particularly, recording sheets composed of a paper support covered on the both sides thereof with polyolefin resin such as polyethylene has recently been widely enlarged since prints using such sheets have high class feeling similar to silver halide photographic prints in the depth, flexibility, smoothness and glossiness.

[0004]

A swelling type ink accepting layer and a porous type ink accepting layer are known as an ink accepting layer which can be provided on a support.

[0005]

The swelling type ink accepting layer is basically constituted of hydrophilic polymer such as polyvinyl alcohol, polyvinyl pyrrolidone and polyethylene oxide. The swelling type ink accepting layer has features such as high glossiness can be obtained, a large amount of ink can be absorbed within

the swellable range of the polymer since swellable polymer is used, and the sheet can be produced at low cost.

[0006]

As a typical example, a recording sheet for an aqueous ink having an ink accepting layer is proposed which contains hydrophilic resin crosslinked by irradiation of ionizing radiation, compare to referred patent document 1. However, there is a problem in that the ink absorbability is lowered when the crosslinked resin is used to absorb the ink in the swelling type ink accepting layer.

[0007]

On the other hand, a porous type ink accepting layer can be produced by several methods, and a typical one of these is a layer constituted by a small amount of hydrophilic polymer and a large amount of micro particles. In such a layer, pores are formed and the ink is absorbed in them. The features of such a layer are that unevenness of printed images occurs; the surface of the printed image is only seemingly dried just after the printing; and both water proofing and ink absorption rate are simultaneously satisfied contrary to that which occurs in the case of swelling type sheet.

[0008]

For example, a method has been proposed in which a coating liquid composed of inorganic sol and an ionizing radiation hardenable compound is coated and dried to prevent occurrence of defect of the coated layer such as mottling or cracking of the coated layer and to improve strength of the layer such as resistance to water and subsequent damage and ink absorption ability, compare to referred patent document 2. However, the technology disclosed in the document is insufficient to improve light fastness of color, weather proofing and damage to the ink accepting layer surface when the ink-jet recording sheet is handled in a rolled form.

[0009]

Referred patent document 1:

Japanese Patent Publication Open to Public Inspection, hereinafter referred to as Japanese Patent O.P.I. Publication, No. 1-286886

[0010]

Referred patent document 2:

Japanese Patent O.P.I. Publication, No. 9-263038

[0011]

[TECHNICAL PROBLEM TO BE DISSOLVED BY THE INVENTION]

The objective of the present invention is to provide an ink-jet recording sheet with high ink absorption, in which

the resistance to color fading by light is excellent; the weather proofing ability is high; and occurrence of cracking in the production processes such as coating and drying and that fractures caused by bending in the course of handling after drying are prevented.

[0012]

[MEANS TO DISSOLVE THE PROBLEMS]

The inventors have found that the above-mentioned object of the invention can be attained by the following constitution.

[0013]

(1) An ink-jet recording sheet comprising a support and an ink accepting layer provided on at least one side of the support wherein the ink accepting layer is a porous ink-accepting layer comprising a hydrophilic binder containing a polymer compound crosslinked by irradiation of ionizing radiation, micro particles, and at least one component selected from the group consisting of (A) a nitrogen-containing compound, (B) a sulfur-containing compound, (C) a polyvalent metal salt and (D) a phenol compound.

[0014]

(2) The ink-jet recording sheet described in (1), wherein the micro particles have an average diameter of from 5 to 200 nm.

[0015]

(3) The ink-jet recording sheet described in (1) or (2), wherein a ratio of the contained micro particles to the hydrophilic binder is from 2 to 50 by weight.

[0016]

(4) The ink-jet recording sheet described in (3), wherein the ratio of the contained micro particles to the hydrophilic binder is from 5 to 15 by weight.

[0017]

(5) The ink-jet recording sheet described in any one of (1) to (4), wherein the polymer compound crosslinked by irradiation by ionizing radiation is a polymer compound formed by crosslinking a hydrophilic resin having a dimer formable photosensitive group formed by irradiation via ionizing radiation.

[0018]

(5) The ink-jet recording sheet described in any one of (1) to (5), wherein the nitrogen-containing compound is at least one selected from the group consisting of a hindered amine

compound, a hydroxylamine compound and a water-soluble aliphatic tertiary amine compound.

[0019]

(7) The ink-jet recording sheet described in any one of (1) to (5), wherein the sulfur compound is a compound represented by Formula 1 or Formula 2:

[0020]

(8) The ink-jet recording sheet described in any one of (1) to (5), wherein the polyvalent metal salt is a water-soluble salt of one selected from the group consisting of cesium, magnesium, aluminum and zirconium.

[0021]

(9) The ink-jet recording sheet described in any one of (1) to (5), wherein the phenol compound is a hindered phenol compound or a hydroquinone diether compound.

[0022]

It is assumed that ink-jet recording sheets exhibiting high ink absorbability, in which the resistance to color fading by light is excellent, weather proofing ability is high, the occurrence of cracking in the production processes such as coating and drying and fractures caused by bending in the course of handling after drying are prevented can be provided by the following reason.

[0023]

Hydrophilic binders crosslinked by irradiation via ionizing radiation are instable in the independent state. However, such binders can be stabilized by being combined with at least one component selected from the group consisting of (A) a nitrogen-containing compound, (B) a sulfur-containing compound, (C) a poly-valent metal salt and (D) a phenol compound, and the light fastness of color and the weather proofing ability of the binders are improved. Usually, the hydrophilic binder is hardened by a crosslinking agent or hardening agent to raise the layer strength by crosslinking. However, problems such as cracking occurring during coating and drying and the fractures due to bending tend to be formed by excessive hardness of the layer when such hardeners are used. On the other hand, ink-jet recording sheet with high ink absorbability and without formation of the cracking and fractures caused by bending can be obtained when the hydrophilic binders contain a polymer compound crosslinked by irradiation via ionizing radiation, which seem to work together when a hardener is used with at least one of the compounds selected from the group consisting of (A) a nitrogen-containing compound, (B) a sulfur-

containing compound, (C) a poly-valent metal salt and (D) a phenol compound.

[0024]

The present invention is described in detail below.

In the invention, the ink accepting layer contains a hydrophilic binder having a specific function, the micro particles are used as filler and has at least one compound selected from the group consisting of (A) a nitrogen-containing compound, (B) a sulfur-containing compound, (C) a poly-valent metal salt and (D) a phenol compound.

[0025]

First, the hydrophilic binder relating to the invention is described.

The hydrophilic binder relating to the invention contains a polymer crosslinked by irradiation via ionizing radiation. Polymer compounds crosslinkable by the ionizing radiation irradiation are water-soluble resins capable of undergoing a crosslinking reaction by irradiation via ionizing radiation such as ultraviolet rays and electron rays. The resin is basically insoluble after the crosslinking reaction. However, the resin has some degree of hydrophilicity after the crosslinking reaction so that the required affinity to ink is sufficiently maintained.

[0026]

Examples of resins capable of crosslinking by irradiation via ionizing radiation include a photo-dimerizable resin, a photo-decomposable resin, a photo-modifying resin and a photo-depolymerizable resin. The photo-dimerizable resins are preferred in the invention. As a photo-dimerizable resin, ones in which a diazo group, a cinnamoyl group, a stilbazonium group or a stilquinolium group is introduced are preferable.

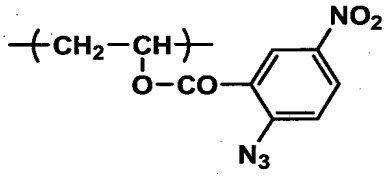
[0027]

Further, it is preferable that the hydrophilic polymer is resin which are dyed with water-soluble dyes such as anionic dyes after photo-crosslinking. Listed as such resins are, for example, resins having a cationic group such as a primary amino group and a quaternary ammonium group, photosensitive resins (being compositions) described, for example, in Japanese Patent Application Open to Public Publications 56-67309, 60-129742, 60-252341, 62-283339, and 1-198615, resins having a group such as an azido group which is converted to an amino group through a curing treatment, while becoming cationic, and photosensitive resins (being compositions) described, for example, in Japanese Patent Application Open to Public Inspection No. 56-67309.

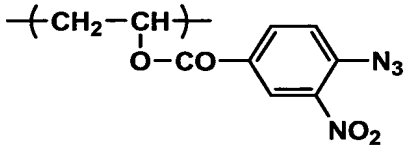
[0028-0032]

In the present invention, preferably employed are photosensitive resins described in Japanese Patent Application Open to Public Inspection No. 56-67309. The aforesaid resins include resin compositions having a 2-azido-5-nitrophenylcarbonyloxyethylene structure represented by Formula (I), described below, or a 4-azido-3-nitrophenylcarbonyloxyethylene structure represented by Formula (II), also described below, in a polyvinyl alcohol structure.

Formula (I)



Formula (II)



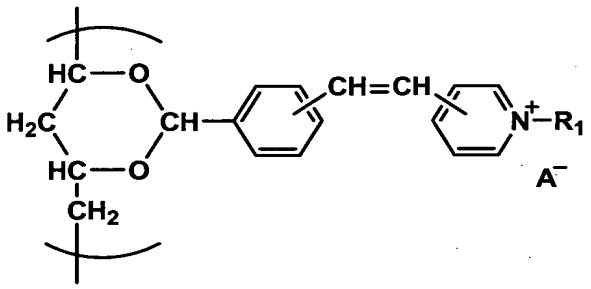
[0033]

Specific examples of the aforesaid resins are described in Examples 1 and 2 of the aforesaid patent publication, while constitution components and their used ratio are described on page 2 thereof.

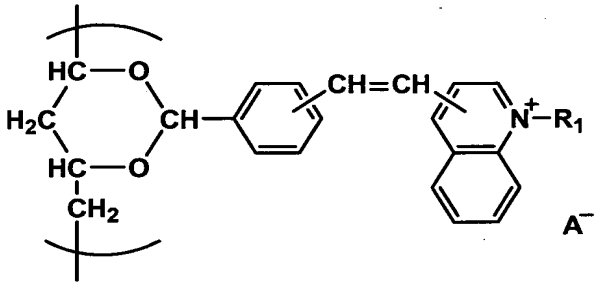
[0034-0036]

Further, Japanese Patent Application Open to Public Inspection No. 60-129742 describes photosensitive resins which include polyvinyl alcohol based resins having the structural units represented by Formula (III) or (IV), described below, in the polyvinyl alcohol structure;

Formula (III)



Formula (IV)



wherein R_1 represents an alkyl group having 1 - 4 carbon atoms, and A^- represents an anion. These are polyvinyl alcohol based resins having structural units comprising a styrylpyridinium (stilbazolium) structure or a styrylquinolinium structure, which are prepared by allowing

polyvinyl alcohol or partially saponified polyvinyl acetate to react with a styrylpyridinium salt or a styrylquinolinium salt. The production method of these is described in Japanese Patent Application Open to Public Inspection No. 60-129742 and is easily produced with reference to the aforesaid patent publication.

[0037]

The ratio of a styrylpyridinium group or a styrylquinolinium group in polyvinyl alcohol having the styrylpyridinium group or the styrylquinolinium group is preferably 0.2 - 10.0 mol percent per polyvinyl alcohol unit. The more photosensitive units are introduced, the higher the speed. When the aforesaid constitution units are introduced into polyvinyl alcohol in an amount over the upper limit, the resulting resins are not easy to dissolve in water. On the other hand, when the ratio is not more than to 0.2 percent, the effects of the present invention are not achieved due to sufficient strength after crosslinking.

[0038]

Further, in the foregoing, polyvinyl alcohol used as a main component may be comprised of acetyl groups which are not partially saponified and the proportion of the acetyl group is preferably less than 30 percent. The degree of

polymerization thereof is preferably about 400 - about 3,000, and a degree of polymerization of 400 or less is not preferred because it is possible to inhibit deterioration of resistivity against folding due to the three dimensional structure density becoming high. Further, when the degree of polymerization is more than 3,000, handling may not be easy because of high viscosity.

[0039]

An aqueous coating composition prepared by mixing such photosensitive resins with fine particles is applied onto at least one side of a support. Thereafter, the resulting coating is cured while exposed to ionizing radiation, whereby an ink-jet recording sheet comprising the porous layer according to the present invention is prepared. Examples of ionizing radiation include electron beams, ultraviolet radiation, α-rays, β-rays, γ-rays, and X-rays. Preferably employed are electron beams and ultraviolet radiation, which do not have the large influence on a human body and are easily handled and thus widely employed in industry.

[0040]

When electron beams are employed, the exposure amount of the aforesaid electron beam is preferably controlled to be in the range of 0.1 - 20 Mrad. An exposure amount of not

less than 0.1 Mrad does not result in sufficient exposure effects. An exposure amount of at not more than 20 Mrad is not preferred because it is able to avoid deteriorating deteriorate supports, especially paper and certain type of plastics. Accepted as electron beam exposure systems are, for example, a scanning system, a curtain beam system, and a broad beam system. Appropriate acceleration voltage during electron beam exposure is 100 - 300 kV. Incidentally, the aforesaid electron beam exposure system exhibits advantages such that, compared to the ultraviolet radiation exposure, higher productivity can be achieved, problems such as unpleasant odor and coloration due to the addition of sensitizers do not occur, and further, uniform crosslinking structures are easily achieved.

[0041]

The aforesaid hydrophilic polymer compounds having the polymerization degree of not less than 300 and the plurality of side chains on the main chain thereof, which are preferably employed in the present invention, are sensitive to, for example, ultraviolet radiation without adding the sensitizers described below and are capable of readily undergoing a crosslinking reaction. Employed as radiation sources of the ultraviolet radiation are UV lamps (e.g., low

pressure, medium pressure, and high pressure mercury lamps having an operating pressure of 0.5 - 1 MPa), xenon lamps, tungsten lamps, and halogen lamps. The intensity of the exposed ultraviolet radiation is preferably about 5,000 - about 8,000 $\mu W/cm^2$. Energy requirement for crosslinking through the side chains is in the range of 0.02 - 20 kJ/cm^2.

[0042]

Further, when ultraviolet radiation is employed, sensitizers may be incorporated in coating compositions. For example, sensitizers such as thioxanthone, benzoin, benzoin alkyl ether xanthone, dimethylxanthone, benzophenone, and 1,1-dichloroacetophenone may be incorporated individually or in combinations of at least two types.

[0043]

Incidentally, when sensitizers are employed, the used amount thereof is customarily controlled to be in the range of 0.2 - 10 percent by weight with respect to the ionizing radiation crosslinkable type polymer compound in the coating composition, and preferably in the range of 0.5 - 5 percent by weight. Further, tertiary amines such as triethanolamine, 2-dimethylaminoethanol, and dimethylaminobenzoic acid may be mixed in coating compositions in an amount of 0.05 - 3

percent by weight with respect to the ionizing radiation type polymer compound.

[0044]

In the invention, the crosslinking reaction of polymer compound capable of crosslinking by irradiation via ionizing radiation is accelerated and the fluidity of the coated layer is inhibited when the coated layer is irradiated by the ionizing radiation in the presence of a hydrophilic solvent. Thus a uniformly coated layer can be formed. Concretely, the coated layer is dried after irradiation via ionizing radiation by evaporating the aqueous solvent principally composed of water. However, a minor or major part of the aqueous solvent may be evaporated in the course of the irradiation via ionizing radiation.

[0045]

The following hydrophilic resin may be used together with the polymer compound capable of crosslinking by irradiation via ionizing radiation as long as the objective properties of the recording sheet of the invention are not degraded.

[0046]

Hydrophilic binders employed in combination are not particularly limited, and any of those, may be employed. For

example, employed may be gelatin, polyvinylpyrrolidone, polyethylene oxide, polyacrylamide, and polyvinyl alcohol. Of these, polyvinyl alcohol is particularly preferred.

[0047]

Polyvinyl alcohol is a polymer whose hygroscopic properties exhibit a relatively small dependence on humidity, and whose contraction stress during coating and drying is also relatively small. As a result, polyvinyl alcohol is excellent in minimizing cracking during coating and drying, which is the problem to be solved by the present invention. Polyvinyl alcohol preferably employed in the present invention includes common polyvinyl alcohol which is prepared by hydrolyzing polyvinyl acetate and also modified polyvinyl alcohol such as polyvinyl alcohol whose terminals have been subjected to cation modification and anion-modified polyvinyl alcohol having an anionic group.

[0048]

The average degree of polymerization of said polyvinyl alcohol prepared by hydrolyzing vinyl acetate is preferably at least 300, and is more preferably from 1,000 to 5,000. The saponification ratio of said polyvinyl alcohol is preferably from 70 to 100 percent, and is more preferably from 80 to 99.5 percent.

[0049]

Said cation-modified polyvinyl alcohol includes, for example, polyvinyl alcohol which has a primary, secondary or tertiary amino group, or a quaternary ammonium group in the main or side chain of said polyvinyl alcohol, as described in Japanese Patent Publication Open to Public Inspection No. 61-10483. Said polyvinyl alcohol is prepared by saponifying the copolymer of an ethylenic unsaturated monomer having a cationic group and vinyl acetate.

[0050]

Examples of ethylenic unsaturated monomer include trimethyl(2-acrylamido-2,2-dimethylethyl)ammonium chloride, N-vinylimidazole, N-vinyl-2-methylimidazole, N-(3-dimethylaminopropyl)methacrylamide, hydroxyethyl trimethylammonium chloride, trimethyl(methacrylamidopropyl)ammonium chloride, and N-(1,1-dimethyl-3-dimethylaminopropyl)acrylamide.

[0051]

The ratio of the monomer having a cationic modifying group in the cationic modified polyvinyl alcohol to vinyl acetate is from 0.1 to 10 mole percent, preferably from 0.2 to 5 mole percent.

[0052]

Examples of anionic modified polyvinyl alcohol include the polyvinyl alcohol having an anionic group described in Japanese Patent O.P.I. Publication No. 1-206088, a copolymer of vinyl alcohol and vinyl compound having a water-solubilizing group described in Japanese Patent O.P.I. Publication Nos. 61-237681 and 63-307979 and a modified polyvinyl alcohol having a water-solubilizing group described in Japanese Patent O.P.I. Publication No. 7-285265.

[0053]

Examples of nonionic modified polyvinyl alcohol include the polyvinyl alcohol derivatives in which a poly(alkylene oxide) group is added to a part of the polyvinyl alcohol described in Japanese Patent O.P.I. Publication No. 7-9758, and a block copolymer of a vinyl compound having a hydrophobic group and vinyl(alcohol) described in Japanese Patent O.P.I. Publication No. 8-25795.

[0054]

Two or more kinds of these polyvinyl alcohols, each different from the others in the polymerization degree or type of modification may be used in combination.

[0055]

Fine particles are described.

Employed as fine particles usable in the present invention may be fine inorganic and organic particles. However, fine inorganic particles are particularly preferred, since high gloss as well as high color density is obtained, and in addition, fine particles are easily prepared.

[0056]

Listed as said inorganic particles may be, for example, white inorganic pigments such as precipitated calcium carbonate, heavy calcium carbonate, magnesium carbonate, kaolin, clay, talc, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, hydrotalcite, aluminum silicate, diatomaceous earth, calcium silicate, magnesium silicate, synthetic non-crystalline silica, colloidal silica, alumina, colloidal alumina, pseudo- boehmite, aluminum hydroxide, lithopone, zeolite, and magnesium hydroxide. Primary particles of said fine inorganic particles may be employed without any further modification, and said inorganic particles may also be employed in the state in which secondary coagulated particles are formed.

[0057]

In the present invention, from the viewpoint of preparing high quality prints utilizing ink jet recording

sheets, preferred as fine inorganic particles are alumina, pseudo-boehmite, colloidal silica, and fine silica particles synthesized employing a gas phase method. Of these, fine silica particles synthesized employing a gas phase method are particularly preferred. Said silica synthesized employing a gas phase method, whose surface is modified with aluminum may be employed. The content ratio of aluminum in the gas phase method silica whose surface is modified with aluminum is preferably from 0.05 to 5 percent by weight with respect to the total silica.

[0058]

The diameter of the inorganic micro particle is preferably not more than 200 nm from the viewpoint of glossiness and color appearance even though particles having any diameter may be used. The particle diameter is preferably not less than 5 nm from the viewpoint of production even though there is no specific limitation to the lower limit of particle diameter. The average diameter of these inorganic micro particles is defined by a simple average or number average of the diameters of 100 randomly selected particles, the averages being obtained by electron microscopic observation of the cross section or the surface of the porous ink accepting layer. The particle diameter is

represented by the diameter of the area of a circle having an area equal to the projection area of an individual particle.

[0059]

Further, from the viewpoint of glossiness as well as color forming properties, the degree of dispersion of fine particles in the porous layer is preferably no more than 0.5. When said degree of dispersion is not more than 0.5, the resulting glossiness as well as color forming properties of the image printed is sufficiently obtained. The degree of dispersion of fine particles, as described herein, refers to the value obtained by dividing the standard deviation of the particle diameter by the average particle diameter which is determined by observing the fine particles of the porous layer in the same manner as for determining the aforesaid average particle diameter.

[0060]

Said fine particles may be located in the porous layer in the form of primary particles which are not subjected to any modification, secondary particles, or higher order coagulated particles. However, said average particle diameter refers to the average diameter of particles which form independent particles in the porous layer when observed with an electron microscope.

[0061]

The content of said fine particles in the water-soluble coating composition for forming the porous layer is preferably from 5 to 40 percent by weight, and is more preferably from 7 to 30 percent by weight.

[0062]

The ratio of micro particles to the hydrophilic binder contained in the ink accepting layer is preferably from 2 to 50 by weight. When the ratio is not less than 2, the space ratio in the porous ink accepting layer is sufficient and the blocking of pores by swelling of excessive hydrophilic binder can be prevented during ink-jet recording. When the ratio is not more than 50, the fractures due to bending cause problems when a thick porous ink accepting layer is applied. Ratio of micro particles to the hydrophilic binder of from 5 to 15 is particularly preferable since the fractures due to bending in the dried layer is prevented.

[0063]

The ink accepting capacity per unit area of the porous ink accepting layer according to the invention is preferably from about 15 to 40 ml/m^2. Absorbing capacity is defined by the volume of bubbles formed when the unit volume of the

coated layer is immersed in water, or by the volume of water to fully saturate the coated layer.

[0064]

Next, (A) the nitrogen-containing compound, (b) the sulfur-containing compound, (C) the polyvalent metal salt, and (D) the phenol derivative relating to the invention are described.

[0065]

(A) Nitrogen-containing compound

As the nitrogen-containing compound, those described in Japanese Patent O.P.I. Publications 2000-263918, 2001-139851, 2001-341418, 2002-19267, 2001-191640, 2000-271499, 62-37181, 62-37182, 62-37183, 61-164989, 59-96987 and 61-146591 can be used. Among these, hindered amine compounds typified by 2,2,6,6-tetramethylpiperidine having a substituent at the 4-site, hydroxylamine compounds and water-soluble aliphatic tertiary amine compounds are cited as particularly preferred nitrogen-containing compound. Concretely, Adecastarb LA-52 produced by Asahi Denka Co., Ltd., Syasorb UV-3346, produced by Sytech Co., Ltd., Sumisoap 577, produced by Sumitomo Kagaku Kogyo Co., Ltd., N,N-bis-sulfoethylhydroxylamine and triethanol amine are cited.

[0066]

The added amount of the nitrogen-containing compound to the porous ink accepting layer is preferably from 0.01 g to 3 g per m^2 of the ink-jet recording sheet, even though the added amount is not specifically limited. When the amount is not more than 3 g, blocking of the pores in the porous ink accepting layer by such a compound is inhibited to maintain the high ink absorbing ability. When the amount is not less than 0.01 g, the effects of the invention are sufficiently enhanced. From such a viewpoint, a compound is preferably used within the range of from 0.1 to 2 g per m^2 of the ink-jet recording sheet.

[0067]

(B) Sulfur-containing compound

As the sulfur-containing compound, those described in Japanese Patent O.P.I. Publications 61-177279, 61-136886, 64-36479, 7-314883, 7-314882, 1-115677, 8-25679, 10-330644, and 2001-170136 can be used. Among these, ones represented by the foregoing Formula 1 or 2 are particularly preferable sulfur-containing compounds.

[0068]

In Formula 1, the alkyl group represented by R or R' is a substituted or unsubstituted alkyl group. Examples of these substituents include a hydroxyl group, an aryl group,

an alkoxyl group, an alkylthio group, an amino group, a mercapto group, a carboxyl group, a sulfo group, an acyl group, a carbamoyl group, a sulfamoyl group, and a halogen atom. Specific examples of compound represented by Formula 1 are shown below.

[0069]

(1-1)

$HOC_2H_4SC_2H_4OH$

(1-2)

$HOC_2H_4SC_2H_4SC_2H_4OH$

(1-3)

$HOC_2H_4SC_2H_4SC_2H_4SC_2H_4OH$

(1-4)

$C_4H_9COOC_2H_4SC_2H_4SC_2H_4OH$

(1-5)

$C_4H_9COOC_2H_4SC_2H_4SC_2H_4OCOC_4H_9$

(1-6)

$C_{12}H_{25}OCOC_2H_4SC_2H_4COOC_{12}H_{25}$

(1-7)

$(C_4H_9SC_2H_4COOCH_2)_2S$

(1-8)

$(C_{12}H_{25}SC_2H_4COOCH_2)_2S$

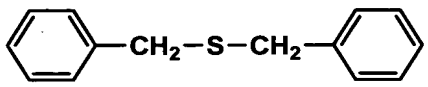
(1-9)

$(HOOCCH_2CH_2)_2S$

(1-10)

$(HOOCCH_2)_2S$

(1-11)



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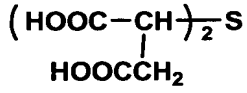
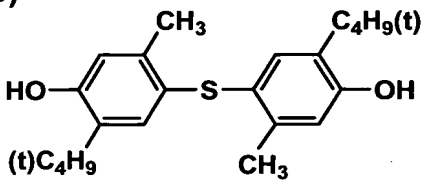


[0070]

(1-13)



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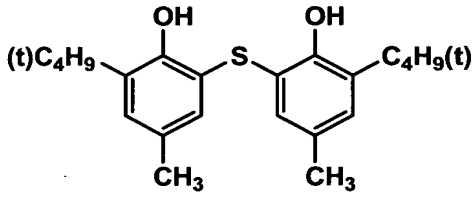

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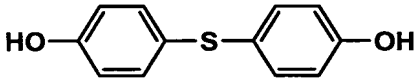

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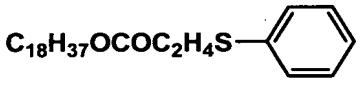

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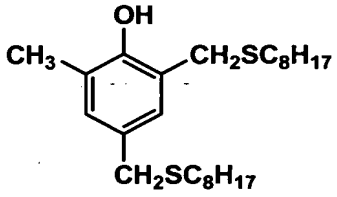

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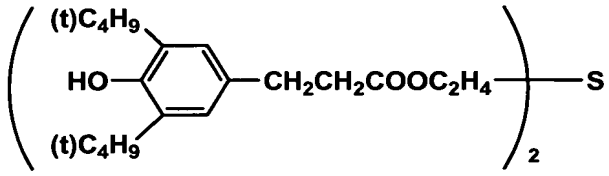

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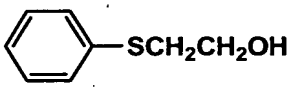


[0071]

Among the foregoing compounds, the water-soluble thioether compounds are preferred. Compounds having at least one water-solubilizing group such as a hydroxyl group or a sulfo group are particularly preferred.

[0072]

In the compounds represented by Formula 2, five- through seven-member rings composed of the group of non-metal atoms represented by X is preferably a five-member azole. Preferable examples of azole rings include single rings such as a pyrrole ring, a pyrazole ring, an imidazole ring, a triazole ring, a tetrazole ring, an oxazole ring, a thiazole ring, a thiadiazole ring, a selenazole ring, and a tellurazole ring, as well as a condensed ring such as an indole ring, an indazole ring, a purine ring, a benzimidazole, a benzotriazole ring, a benzoxazole ring, a benzothiazole ring, a naphthoimidazole ring, and a naphthothiazole ring. Other than the above, six-member rings such as a pyridine ring, a pyrimidine ring, a pyrazine ring, a pyridazine ring, and an s-triazine and their condensed rings such as a quinoline ring, an iso-quinoline ring, a phthalazine ring, a quinoquizaline ring, and a quinazoline

ring, and seven-member rings such as azepine and benzodiazepine are cited as preferable ones.

[0073]

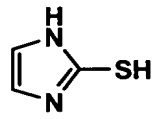
The foregoing rings each may have a substituent. Examples of the substituent include an alkyl group, an alkenyl group, an aryl group, an alkoxyl group, an aryloxy group, an alkylthio group, an arylthio group, a hydroxyl group, an amino group, a mercapto group, a carboxyl group, an acyl group, a carbamoyl group, a sulfamoyl group, a halogen atom, and a cyano group. Each of these substituents may further have a substituent.

[0074]

Specific examples of the compounds represented by Formula 2 are shown below.

[0075]

(2-1)



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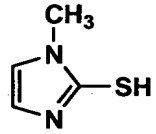

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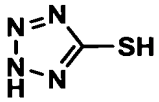

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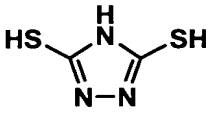

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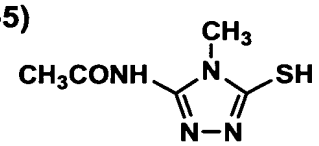

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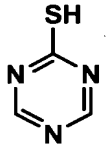

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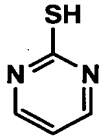

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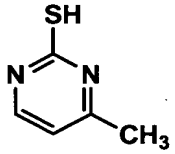
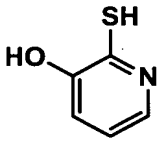


[0076]

(2-9)



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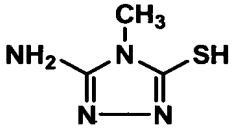

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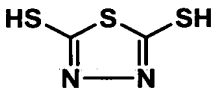

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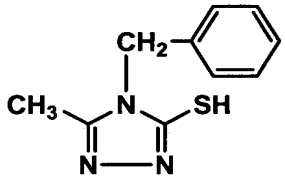

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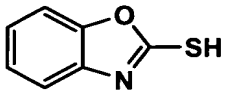

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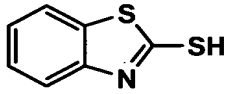

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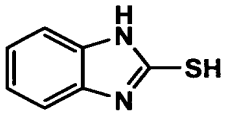

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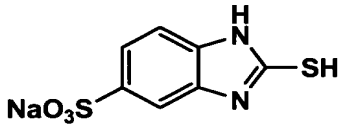

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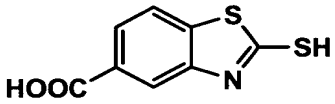

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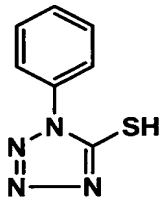

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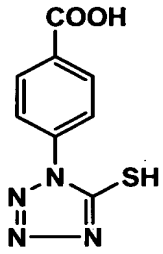

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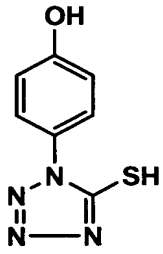

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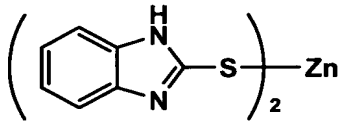

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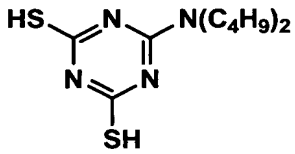


[0077]

The added amount of the sulfur-containing compound to the porous ink accepting layer is preferably from0.01 to 3.0 g per m^2 of the ink-jet recording sheet, even though there is no specific limitation of the added amount. When the amount is no more than 3 g, blocking of pores in the porous ink accepting layer by such compounds is inhibited so as to maintain the high ink absorbing ability. When the amount is not less than 0.01 g, the effects of the invention are sufficiently enhanced. From such a viewpoint, the compound is preferably used within the range of from 0.1 to 2 g per m^2 of the ink-jet recording sheet.

[0078]

(C) Polyvalent metal salt

The polyvalent metal salt is a salt of di- or more-valent metal, but a salt of di- through tetra-valent metals is preferred. For example, ones described in Japanese Patent O.P.I. Publications 7-149037, 61-43593, 55-53591, 56-86789, 58-94491, 59-155088, 59-96988, 60-46288, 60-67190, 60-189480, 61-10484, 61-57379, 8-25794, 4-7189, 8-118788, 9-1769995, 11-321099, 10-226153, 2001-130126, 2001-138622, 2001-238340, 2001-334742 and 2002-103786 may be used as a polyvalent metal salt. Preferable metal salts are water-soluble salts of

cesium, magnesium, aluminum, and zirconium. Particularly preferable metal salts are zirconium salts, zirconium chloride, zirconium nitrate, zirconium acetate, and zirconium tetrachloride.

[0079]

The added amount of the polyvalent metal salt to the porous ink accepting layer is within the range of approximately from 0.1 to 10 millimoles per m^2 of the ink-jet recording sheet. When the added amount is less than 0.1 millimoles, the desired effect of the salt is inadequate, and when the amount exceeds 10 millimoles, coagulation of the dye is accelerated and bronzing of the surface tens to occur. Particularly preferred added amount is from 0.2 to 2 millimoles per m^2 of the ink-jet recording sheet.

[0080]

(D) Phenol compounds

As the phenol compound, those described in Japanese Patent O.P.I. Publications 2000-233655, 1-18684, 1-95091, 57-74192, 57-87989, 64-36480, and 1-18684 can be used. As preferable phenol compounds, hindered phenol compounds in which each of the molecules of which at least one of the ortho-sites of the hydroxyl group is substituted by a tertiary alkyl group, and hydroquinone diether compounds are

cited. Concretely, the followings are usable: Sumilizer BHT, Sumilizer MDP-S, Sumilizer GM, and Sumilizer BBM-S, each produced by Sumitomo Kagaku Kogyo Co., Ltd.; Irganox 1076, Irganox 565, Irganox 1520, and Irganox 245, each produced by Ciba Specialty Chemicals Co., Ltd.; Adecastarb AO-80 and Adecastarb AO-23, each produced by Asahi Denka Kogyo Co., Ltd.; and 2,5-di(t)pentylhydroquinone-1,4-dioctyl ether.

[0081]

The added amount of the phenol compound to the porous ink accepting layer is preferably from 0.01 to 3 g per m^2 of the ink-jet recording sheet, even though the added amount is not specifically limited. When the amount is not more than 3 g, blocking of the space in the porous ink accepting layer by such compound is inhibited so as to maintain high ink absorbing ability. When the amount is not less than 0.01 g, the effects of the invention are sufficiently enhanced. From such viewpoint, the compound is preferably used within the range of from 0.1 to 2 g per m^2 of the ink-jet recording sheet.

[0082]

As the support to be used in the invention, known supports usually used for ink-jet recording sheet are commonly usable. Supports to be used for the ink-jet

recording sheet can be roughly classified into supports, each of which is ink absorbable itself such as paper and that having an ink accepting layer thereon. Prints exhibiting high quality feeling can not be obtained by the former since high image density cannot be obtained and considerable wrinkles occur because the ink is directly absorbed into the support.

[0083]

In contrast, an ink-jet print image with a high quality feel can be obtained by ink-jet recording sheets composed of an ink non-absorbable support and an ink accepting layer provided thereon since such sheets do not have the foregoing drawbacks. Accordingly, the preferable support is a water non-absorbable support.

[0084]

For example, a transparent or opaque film made from polyester resin, diacetate resin, triacetate resin, polyolefin resin, acryl resin, polycarbonate resin, polyvinyl chloride resin, polyimide resin, cellophane or celluloid, and resin coated paper so-called RC paper, which is paper covered with a polyolefin resin layer on both side thereof, are usable.

[0085]

For the purpose of enhancing the adhesion between said various supports and the ink receiving layer, it is preferable that prior to coating said ink receiving layer, said supports are subjected to a corona discharge treatment, as well as a subbing treatment. Further, the ink-jet recording sheets of the present invention are not necessary to be white and may be tinted.

[0086]

Preferable examples of the supports are transparent polyester film, opaque polyester film, opaque polyolefin resin film and paper support laminated with polyolefin resin on both sides. It is particularly preferable that employed as the ink-jet recording sheets of the present invention be polyethylene laminated paper supports. Said polyethylene laminated paper supports will now be described.

[0087]

Base paper, employed in said paper supports, are made employing wood pulp as the main raw material, if necessary, together with synthetic pulp such as polypropylene and synthetic fiber such as nylon and polyester. Employed as said wood pulp may be any of LBKB, LBSP, NBKP, NBSP, LDP, NDP, LUKP, or NUKP. It is preferable that LBKP, NBSP, LBSP, NDP, and LDP, which are comprised of shorter fiber, are

employed in a greater amount. However, the ratio of LBSP and/or LDP is preferably from 10 to 70 percent by weight.

[0088]

Preferably employed as said pulp is chemical pulp (sulfate pulp and sulfite pulp). Further, also useful is pulp which has been subjected to a bleach treatment to increase its whiteness.

[0089]

Into said base paper suitably incorporated may be sizing agents such as higher fatty acids and alkylketene dimers; white pigments such as calcium carbonate, talc, and titanium oxide; paper strength enhancing agents such as starch, polyacrylamide, and polyvinyl alcohol; optical brightening agent; moisture maintaining agents such as polyethylene glycols; dispersing agents; and softeners such as quaternary ammonium salts.

[0090]

The degree of water freeness of pulp employed for paper making is preferably from 200 to 500 ml under CSF Specification. Further, the sum of weight percent of 24-mesh residue and weight percent of 42-mesh calculated portion regarding the fiber length after beating, specified in JIS-P-8207, is preferably between 30 and 70 percent. Further, the

weight percent of 4-mesh residue is preferably 20 percent by weight or less.

[0091]

The weight of said base paper is preferably from 30 to 250 g/m^2, and is most preferably from 50 to 200 g/m^2. The thickness of said base paper is preferably from 40 to 250 μm.

During the paper making stage or after paper making, said base paper may be subjected to a calendering treatment to result in excellent smoothness. The density of said base paper is generally from 0.7 to 1.2 g/m^3 (JIS-P-8118). Further, the stiffness of said base paper is preferably from 20 to 200 g under the conditions specified in JIS-P-8143. Surface sizing agents may be applied onto the base paper surface. Employed as said surface sizing agents may be the same as those above, capable of being incorporated into said base paper. The pH of said base paper, when determined employing a hot water extraction method specified in JIS-P-8113, is preferably from 5 to 9.

[0092]

Polyethylene, which is employed to laminate both surfaces of said base paper, is mainly comprised of low density polyethylene (LDPE) and/or high density polyethylene

(HDPE). However, other LLDPE or polypropylene may be partially employed.

[0093]

Specifically, as is generally done with photographic paper, the polyethylene layer located on the ink receiving layer side is preferably constituted employing polyethylene into which rutile or anatase type titanium oxide is incorporated so that opacity as well as whiteness is improved. The content ratio of said titanium oxide is generally from 1 to 20 percent by weight with respect to polyethylene, and is more preferably from 2 to 15 percent by weight.

[0094]

It is possible to employ said polyethylene coated paper as glossy paper. Further, in the present invention, it is possible to employ polyethylene coated paper with a matt or silk surface, as obtained in the conventional photographic paper, by carrying out an embossing treatment during extrusion coating of polyethylene onto said base paper.

[0095]

The used amount of polyethylene on both surfaces of said paper is selected so as to optimize the layer thickness of a water based coating composition as well as curling at

low and high humidity after providing a back layer. The thickness of the polyethylene layer on the side onto which the water based coating composition in accordance with the present invention is applied, is preferably in the range of 20 to 40 μm, while the thickness of the polyethylene layer on the opposite side is preferably in the range of 10 to 30 μm.

[0096]

Further, it is preferable that said polyethylene coated substrate exhibits the characteristics described below.

[0097]

(1) Tensile strength is preferably from 20 to 300 N in the longitudinal direction and from 10 to 200 N in the lateral direction, in terms of the strength specified in JIS P 8113.

(2) Tear strength is preferably from 0.1 to 2 N in the longitudinal direction and from 0.2 to 2 N in the lateral direction in terms of the tear strength specified in JIS P 8116.

(3) Compression elasticity is no less than 1,030 N/cm^2.

(4) Bekk surface smoothness is preferably at least 500 seconds under conditions specified in JIS P 8119, however so-called embossed papers may exhibit less than that.

(5) Bekk rear surface smoothness is preferably from 100 to 800 seconds under conditions specified in JIS P 8119.

(6) Opacity is preferably no more than 20 percent and is most preferably no more than 15 percent in terms of the transmittance of light in the visible region, which is determined under conditions of parallel light incidence/diffused light transmission.

(7) Whiteness is preferably at least 90 percent in terms of Hunter's brightness specified in JIS P 8123. Further, when measurement is carried out utilizing JIS Z 8722 (non-fluorescence) and JIS Z 8717 (incorporation of fluorescent agents) and the color is represented utilizing the color specification specified in JIS Z 8730, it is preferable that L* = 90 to 98, a* = -5 to +5, and b* = -10 to +5.

[0098]

For the purpose of enhancing adhesion to the ink receptive layer, a subbing layer is preferably provided on the ink receptive layer side of said substrate. Binders for said subbing layer are preferably hydrophilic polymers such as gelatin, polyvinyl alcohols, and latex polymers having a Tg of -30 to 60 °C. Said binders are employed in an amount of 0.001 to 2 g per m^2 of the recording sheet. For the purpose of minimizing static charge, a small amount of

antistatic agent such as cationic polymers, conventionally known in the art, may be incorporated.

[0099]

For the purpose of improving slipping properties as well as electrification characteristics, a back layer may be provided on the surface opposite the ink receptive layer of said substrate. Binders for said back layer are preferably hydrophilic polymers such as gelatin, polyvinyl alcohols, and latex polymers having a Tg of -30 to 60 °C. Further, also incorporated may be antistatic agents such as cationic polymers, various types of surface active agents, and in addition, about 0.5 to about 20 μm matting agents. The thickness of said backing layer is from about 0.1 to about 1 μm. However, when said backing layer is provided to minimize curling, its thickness is to be from about 1 to about 20 μm. Further, said backing layer may be comprised of at least two layers.

[0100]

When said subbing layer, as well as said back layer, is coated, surface treatments such as a corona treatment or a plasma treatment applied onto the substrate surface are preferably employed in combination.

[0101]

Various types of additives can be incorporated into the water-soluble coating composition which forms said porous layer. Listed as said additives are, for example, cationic mordants, cross-linking agents, surface active agents (being cationic, nonionic, anionic, or amphoteric), background color modifiers, optical brighteners, antiseptics, viscosity modifiers, low-boiling-point organic solvents, high-boiling-point organic solvents, latex emulsions, anti-discoloring agents, UV absorbers, multivalent metallic compounds, (being water-soluble or water-insoluble), matting agents, and silicone oil. Of these, cationic mordants are preferred to enhance waterfastness as well as moisture resistance.

[0102]

Employed as said cationic mordants are polymer mordants having a primary, secondary, or tertiary amino group or a quaternary ammonium salt group. Of these, polymer mordants having a quaternary ammonium salt group are preferred, which result in minimal discoloration as well as minimal degradation of lightfastness during storage, and exhibit sufficiently high mordant capability toward dyes. Said preferred mordants are prepared as either homopolymers of monomers having said quaternary ammonium salt group or

copolymers, and condensation polymers of said monomers with other monomers.

[0103]

Further, it is particularly preferred to incorporate cross-linking agents of hydrophilic binders. The cross-linking agent is able to be comprised in the porous layer or to overcoat the dried porous layer. By employing said cross-linking agents, the waterresistance of the porous layer is enhanced, and in addition, the ink absorbing rate is also enhanced during ink jet recording due to the fact that the swelling of said hydrophilic binders is retarded.

[0104]

Cross-linking agents may be employed, which include inorganic cross-linking agents (for example, chromium compounds, aluminum compounds, zirconium compounds, and boric acids), and organic cross-linking agents (for example, epoxy based cross-linking agents, isocyanate based cross-linking agents, aldehyde based cross-linking agents, N-methylol based cross-linking agents, acryloyl based cross-linking agents, vinyl sulfone based cross-linking agents, active halogen based cross-linking agents, carbodiimide based cross-linking agents, and ethyleneimine based cross-linking agents). The content ratio of said cross-linking agents is commonly from

about 1 to 50 percent by weight with respect to the hydrophilic binder, and is preferably from 2 to 40 percent by weight.

[0105]

When said hydrophilic binders are comprised of polyvinyl alcohols and fine articles are comprised of silica, particularly preferred as cross-linking agents are inorganic cross-linking agents containing element of 3A, 3B, 4A or 4B in Periodic Table such as boric acids and zirconium compounds, as well as epoxy based cross-linking agents.

[0106]

The ink jet recording medium is produced employing a method in which constitution layers comprising an ink absorptive layer are individually or simultaneously applied onto a support, employing a method which is appropriately selected from methods known in the art, and subsequently dried. Preferably employed coating methods include, for example, a roll coating method, a rod bar coating method, an air knife coating method, a spray coating method, a curtain coating method, a slide bead coating method employing a hopper, described in U.S. Patent Nos. 2,761,419 and 2,761,791, or an extrusion coating method.

[0107]

The viscosity of each of the coating liquids during simultaneously multi-layer coating is preferably from 5 to 100 mPa·s, more preferably from 10 to 50 mPa·s, for a slide bead coating method, and preferably from 5 to 1200 mPa·s, more preferably from 25 to 500 mPa·s, for a curtain coating method.

[0108]

The viscosity of the coating liquid at 15 °C is preferably not less than 100 mPa·s, more preferably from 100 to 30,000 mPa·s, further preferably from 3,000 to 30,000 mPa·s, and most preferably 10,000 to 30,000 mPa·s.

[0109]

Just after coating, the ionizing radiation is irradiated to the coated layer in the presence of a hydrophilic solvent to result in crosslinking and to form a uniform coated layer. Then the coated layer is dried to form the porous ink accepting layer having pores.

[0110]

The porous ink accepting layer related to the invention may be constituted as a single layer or multi-layers. In the case of a multi-layer, it is preferable to simultaneously coat all layers for lower the production cost.

[0111]

It is preferable during coating and drying that the coating liquids are each heated to 30 °C or more and simultaneously coated, after which the coated layer is once cooled by 1-15 °C and dried at 10 °C or more. The coating liquids are preferably prepared, coated and dried at a temperature not more than the Tg of the thermoplastic resin so that the thermoplastic resin contained in the surface layer does not form a film in the course of the preparation, coating and drying of the liquids. It is more preferable to perform the drying at a condition within the range of a wet bulb temperature of from 5 to 50 °C and a surface temperature of from 10 to 50 °C. The cooling just after the coating is preferably performed by a horizontal setting method from the viewpoint of uniformity of the coated layer.

[0112]

[EXAMPLES]

The invention is described below referring Examples. However, the invention is not limited to the examples. In the examples, "%" is "% by weight" as long as no specific description is attached.

[0113]

Preparation of ink-jet recording sheet

Preparation of Ink-jet Recording Sheet 1 (Comparative sample)

To 100 kg of 25% dispersion of gas phase method silica (Aerosil 300 produced by Nihon Aerosil Co., Ltd., averaging 7 nm diameter of primary particles) which has a pH of 4.0 and contains 1% of ethanol, and is preliminary uniformly dispersed, 50 kg of a 10% aqueous solution of photo-crosslinkable polyvinyl alcohol, in which a stilbazolium group is introduced, (SPP-SHR produced by Toyo Gosei Kogyo Co., Ltd., with the polymerization degree of the main chain PVA being 2300, and the saponification degree 88%) was added while stirring, and Surfactant S-1 was subsequently added.

[0114]

Then the mixture was dispersed by a high pressure homogenizer at 3000N/cm^2 and filtered through Ball filter, TCP-30 having a filtering accuracy of 30 μm, manufactured by Advantec Toyo Kaisha, Ltd., and made up to 200 liters with purified water to obtain Coating Liquid 1.

[0115]

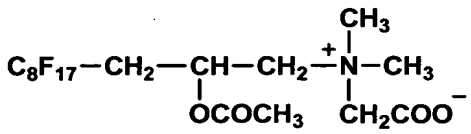
The above Coating Liquid 1 was coated on a paper support covered with polyethylene containing 6% of anatase type titanium oxide on both sides so that the wet layer thickness was 170 μm.

[0116]

After the coating, the coated layer was irradiated by UV rays at an energy amount of 2 kJ/cm^2. Then the surface of the ink accepting layer was air dried at 80 °C to obtain Ink-jet Recording Sheet 1.

[0117]

Surfactant S-1



[0118]

Preparation of Ink-jet Recording Sheet 2 (Inventive Sample)

Ink-jet Recording Sheet 2 was prepared in the same manner as Ink-jet Recording Sheet 1 except that added was 10 kg of a 10% aqueous solution of polyarylamine hydrochloride PAA-HCL-10L, produced by Nitto Boseki Co., Ltd.

[0119]

Preparation of Ink-jet Recording Sheet 3 (Inventive Sample)

Ink-jet Recording Sheet 2 was prepared in the same manner as Ink-jet Recording Sheet 1 except that added was 5 kg of a 10% aqueous solution of sulfur-containing compound 1-2.

[0120]

Preparation of Ink-jet Recording Sheet 4 (Inventive Sample)

Ink-jet Recording Sheet 4 was prepared in the same manner as Ink-jet Recording Sheet 1 except that added was 10 kg of a 5% aqueous solution of hindered amine compound Adecastab LX-332 produced by Asahi Denka Kogyo Co., Ltd.

[0121]

Preparation of Ink-jet Recording Sheet 5 (Inventive Sample)

Ink-jet Recording Sheet 5 was prepared in the same manner as Ink-jet Recording Sheet 1 except that added was 9 kg of a 5% aqueous solution of hindered phenol compound Adecastab LX-802 produced by Asahi Denka Kogyo Co., Ltd.

[0122]

Preparation of Ink-jet Recording Sheet 6 (Inventive Sample)

Ink-jet Recording Sheet 6 was prepared in the same manner as Ink-jet Recording Sheet 1 except that added was 1.5 kg of a 10% aqueous solution of zirconium acetate Zircosol ZA produced by Asahi Denka Kogyo Co., Ltd.

[0123]

Preparation of Ink-jet Recording Sheet 7 (Comparative Sample)

Ink-jet Recording Sheet 7 was prepared in the same manner as Ink-jet Recording Sheet 2 except that the photo-crosslinkable polyvinyl alcohol derivative was replaced by a 10% aqueous solution of polyvinyl alcohol, PVA235, produced of Kuraray Co., Ltd.

[0124]

Preparation of Ink-jet Recording Sheet 8 (Inventive Sample)

Ink-jet Recording Sheet 8 was prepared in the same manner as Ink-jet Recording Sheet 3 except that 10 kg of the 50 kg of 10% aqueous solution of the photo-crosslinkable polyvinyl alcohol derivative was replaced by a 10% solution of polyvinyl alcohol, PVA235, produced by Kuraray CO., Ltd.

[0125]

Preparation of Ink-jet Recording Sheet 9 (Comparative Sample)

Ink-jet Recording Sheet 9 was prepared in the same manner as Ink-jet Recording Sheet 7 except that 500 g of boric acid and 400 g of borax were added.

[0126]

Preparation of Ink-jet Recording Sheet 10 (Inventive Sample)

Ink-jet Recording Sheet 10 was prepared in the same manner as Ink-jet Recording Sheet 2 except that 80 kg of a 10% aqueous solution of the photo-crosslinkable polyvinyl alcohol derivative was added.

[0127]

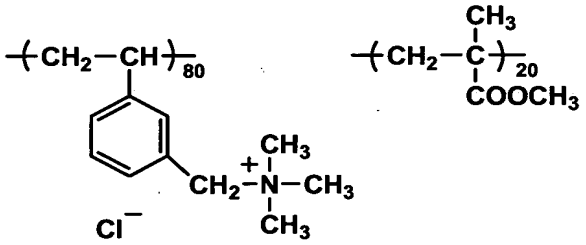
Preparation of Ink-jet Recording Sheet 11 (Inventive Sample)

Ink-jet Recording Sheet 11 was prepared in the same manner as in Ink-jet Recording Sheet10 except that a 3% aqueous solution of cationic polymer P-1 having a molecular

weight of 10,000 was coated on the dried coated layer to a wet thickness of 30 μm.

[0128]

P-1



[0129]

Evaluation of characteristics of the ink-jet recording sheet

Each of the above-prepared ink-jet recording sheets was subjected to evaluation of photo-fading, weather resistivity of the binder, cracking of the layer, fracturing of the layer caused by bending, and ink absorbability.

[0130]

Evaluation on photo-fading

A solid cyan monochromatic image was printed on an ink-jet recording sheet for the evaluation and the printed image was stand for 3 months under ambient room light. The photo fading was represented by the remaining ratio of the optical density of the image after standing to that before standing. A larger value corresponds to a high remaining ratio and good photo-fading resistive property.

[0131]

A: 0.95 or more

B: 0.85 - less than 0.95

C: 0.75 - less than 0.85

D: less than 0.75

Evaluation of weather resistivity

The image was allowed to stand just after printing for 12 hours at 40 °C and a high relative humidity of 70%, and the condition of the surface was visually observed. Alternatively, the printed image was allowed to stand for 12 hours in a Xe Fade-o-Meter (70,000 lux) after which the printed surface was visually observed.

[0132]

A: No cracking was observed on the printed surface.

B: Slight racking was observed on the printed surface.

C: Cracking was apparent on the printed surface.

Evaluation of layer cracking

The number of cracks each having a length of at least 0.2 mm per 10 x 10 cm^2 of the ink-jet recording sheet was counted and classified into the four following ranks.

[0133]

A: Not more than 3 (No problem for practical use)

B: From 4 to 10 (No problem for practical use)

C: From 11 to 19 (Problems were raised for practical use)

D: 20 or more (Problems were raised for practical use)

Evaluation of fracturing caused by bending

The ink-jet recording sheet was conditioned for 3 hours at a temperature of 23 °C and a relative humidity of 10%, then the surface of the ink accepting layer was heated by 150 °C and immediately wound onto stainless steel rods each having a diameter of 10, 15 and 20 mm so that the surface of the ink accepting layer was to be out side. Then noted was the diameter of the rod on which fractures of the ink accepting layer was caused.

[0134]

A: No fracture occur on the 10 mm rod (No problem for practical use)

B: Fractures occur on the 10 mm rod (No problem for practical use)

C: Fractures occur on the 15 mm rod (Problems were raised in practical use.)

D: Fractures occur on the 20 mm rod (Problems were raised in practical use.)

Evaluation on ink absorbability

A solid blue image was printed on each of the ink-jet recording sheets by Ink-jet Printer PM950C, manufactured by Seiko-Epson Co,. Ltd. The printed area was visually observed and evaluated according to the following norm.

[0135]

Incidentally, no sample was classified as rank D in these examples.

[0136]

A: No unevenness in the printed area was observed. (No problem for practical use)

B: Slight unevenness in the printed area was observed. (No problem for practical use)

C: Apparent unevenness in the printed area was observed. (Problems were raised for practical use)

D: Unevenness was observed in almost all the printed area. (Problems were raised for practical use)

Results of the evaluation are shown in Table 1.

[0137]

Table 1

Sample No.	Photo-fading	Weather resistivity of binder		Cracking of the layer	Fractures of the layer caused by bending	Ink absorba-bility	Re-marks
		Xe irradia-tion	High humidity				
1	C	B	B	C	C	A	Comp.
2	A	A	A	A	A	A	Inv.
3	B	A	A	B	A	A	Inv.
4	A	A	A	A	B	A	Inv.
5	B	A	A	A	B	A	Inv.
6	B	A	A	B	A	A	Inv.
7	D	C	C	D	D	C	Comp.
8	B	A	A	A	A	A	Inv.
9	C	B	B	C	C	A	Comp.
10	B	A	A	B	B	B	Inv.
11	B	A	A	B	B	B	Inv.

Comp.; Comparative Inv.; Inventive

[0138]

In Table 1, "Sample No." is the number of the ink-jet recording sheet. "Xe irradiation" shows the evaluation results after standing for 12 hours in an Xe Fade-o-Meter, and "High humidity" shows the evaluation results after standing for 12 hours under a relative humidity of 70%.

[0139]

It can be seen from the results shown in Table 1 that the ink-jet recording sheets of the invention were excellent

in resistance of photo-fading of color and caused no problem for practical use regarding all aspects including weather resistivity of the binder, cracking of the layer, the fracturing caused by bending of the layer, and the ink absorbability.

[0140]

[ADVANTAGE OF THE INVENTION]

An ink-jet recording sheet with high ink absorbability can be provided by the invention, which is excellent in resistance of photo-fading of color and resistance to cracking during the production process (coating and drying) and resistance to fracturing by bending by handling after drying.

[NAME OF DOCUMENT] ABSTRACT

[SUMMARY]

[OBJECTIVES OF THE INVENTION]

To provide an ink-jet recording sheet with high ink absorption, in which the resistance to color fading by light is excellent; the weather proofing ability is high; and occurrence of cracking in the production processes such as coating and drying and that fractures caused by bending in the course of handling after drying are prevented.

[MEANS TO DISSOLVE THE PROBLEMS]

An ink-jet recording sheet comprising a support and an ink accepting layer provided on at least one side of the support wherein the ink accepting layer is a porous ink-accepting layer comprising a hydrophilic binder containing a polymer compound crosslinked by irradiation of ionizing radiation, micro particles, and at least one component selected from the group consisting of (A) a nitrogen-containing compound, (B) a sulfur-containing compound, (C) a polyvalent metal salt and (D) a phenol compound.

[SELECTED DRAWINGS] None